Understanding Corrosion Mechanisms in Oxy-Fired Systems

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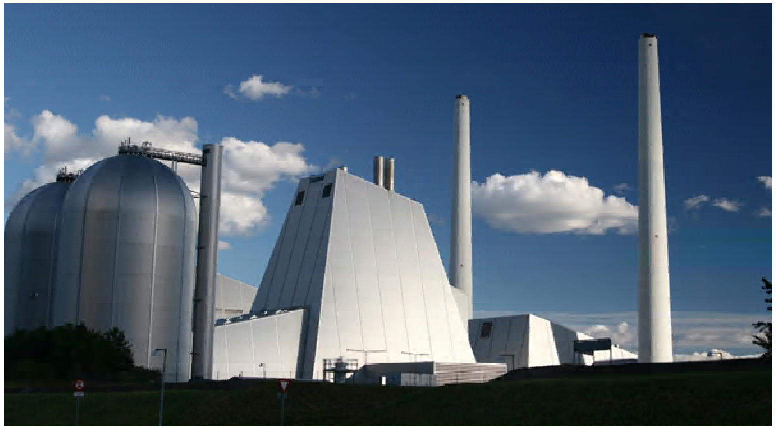
12MWh/yr per U.S. resident

Where will it come from?

coal?

how?

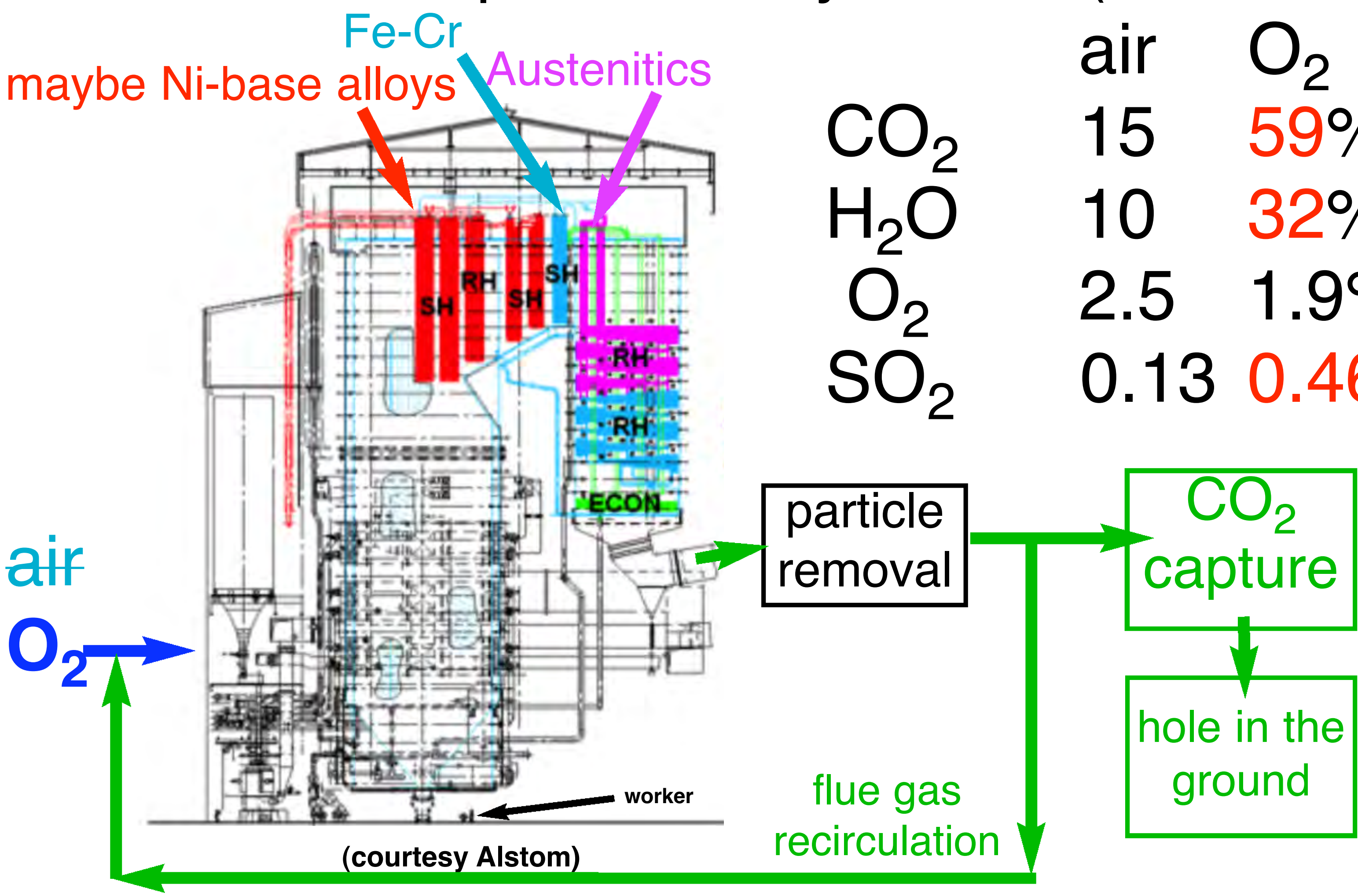
vs.



Literature - focus on worst condition

Several studies published by Alstom (Bordenet)

	air	O_2
CO_2	15	59%
H_2O	10	32%
O_2	2.5	1.9%
SO_2	0.13	0.46%



Germany: 30MW oxy-fired pilot plant (Alstom)

FutureGen 2.0: first major U.S. demonstration

Current Tasks & Timeline

1. Steam/gas corrosion (no ash)
2. Fireside corrosion (with ash)
3. Environment-mechanical property effect
   - effect of steam on creep
4. Coatings (effect on mechanical properties)
   - lower cost fireside coatings
   - TTU subcontract (fabrication and model)
5. Management

A. ~600°C ferritic/martensitic steels (FY10-11)

B. ~650°-700°C austenitic steels

C. ~700°-750+°C Ni-base alloys
   - creep testing at 800°C (FY11)

What’s different here?

Many previous & current studies of oxy-firing & CO_2

- “Oxy” worse: Speigel (2006) + Corvino (2008)
- Complicated: boiler OEMs have advantage
- CO_2 effect: Jülich, U. Pitt & Australia (Young)

Issues with fireside corrosion experiments:

Different experimental conditions (if published)

1000h vs. 10 x 100h (ash re-supply)

Ash/gas/temp. variables

Use of Pt catalyst (SO_2/SO_3)

* Evaluate experimental parameters

Typically, only commercial alloys evaluated

Prior work showing Cu-containing alloy attacked

Was it an effect of Cu or other element(s)?

* Model alloys to better understand composition

Not just commercial alloys

Model alloys: better composition understanding

Ni Content (wt.%)

Cr Content (wt.%)	0		10		15	20	25	30	35	45
15	X									
16		N	O	N	O	O	O	O		
18		N	O	N	O	O	O	O	(2001 set)	
20	X	N	O	N	O	O	O	O		
25		(347mods.)					X		X	X
30	N					(overlay coatings)			→ 622,625	
35	(new)						X		X	X
40	N									

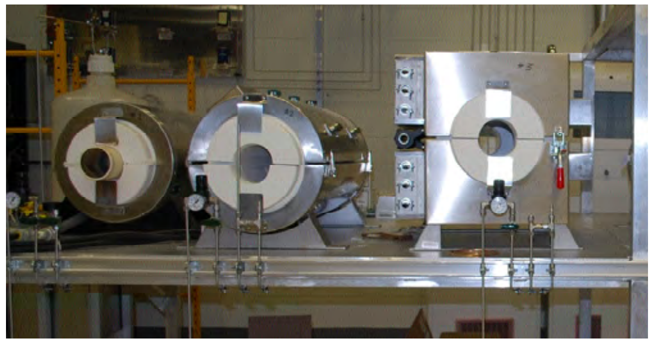
chromizing

Alloy 33

Cast 400g, hot-roll to 8mm: cut coupons & rods

Corrosion testing w/o ash

Determine effect of higher CO_2,



17bar or 1bar

gas only, no ash
- H_2O only
- Ar-50%CO_2*
- H_2O-50%CO_2*

(*CO_2+1500ppmO_2)

Synthetic ash: 30%Fe_2O_3-30%Al_2O_3-30%SiO_2-5%Na_2SO_4-5%K_2SO_4

Gas: N_2-CO_2-H_2O-O_2-SO_2

Temperature: 600°C

Time: 500h (1 cycle)

Porous alumina

Continuing to establish methodology + procedure

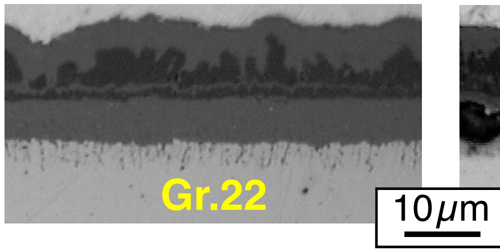
H_2O-SO_2 gases corrode the endcaps!

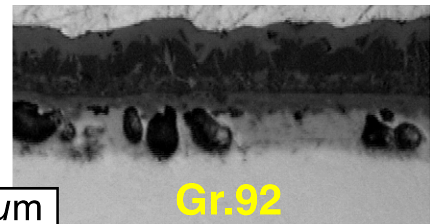
Summary: Gas only exposure

1. 550°C steam 17bar: completed 5kh
   bring 600°-800°C data set back to "now"
2. 600°C: completed 2kh each
   a. steam 1 bar
   b. Ar-50%CO_2-0.15O_2
      - 1500ppmO_2 as buffer
   c. 50%CO_2-0.15O_2-50%H_2O
3. 600°C: coupons in "ash" furnaces w/SO_2
4. 800°C steam 17bar: USC follow on
5. 650°C (starting now, focus austenitics)
   - 3 gases to repeat 600°C

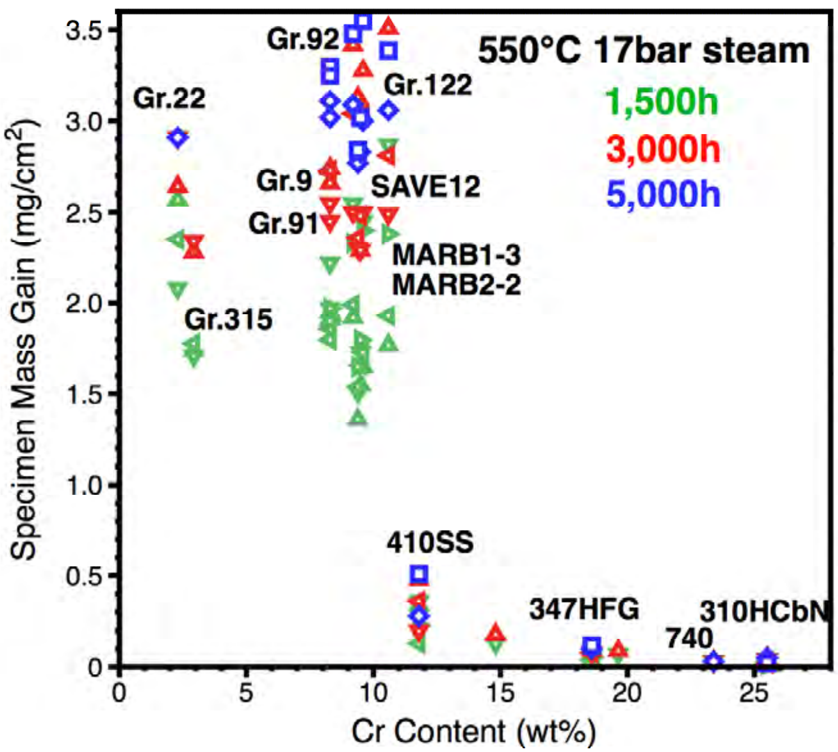
~12%Cr needed at 550°C

For protective behavior at 17bar steam

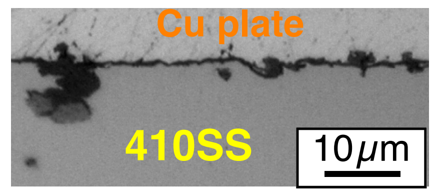




dual oxide layer



2,000 h 550°C



Surprisingly, little difference in 2.25-11%Cr steels

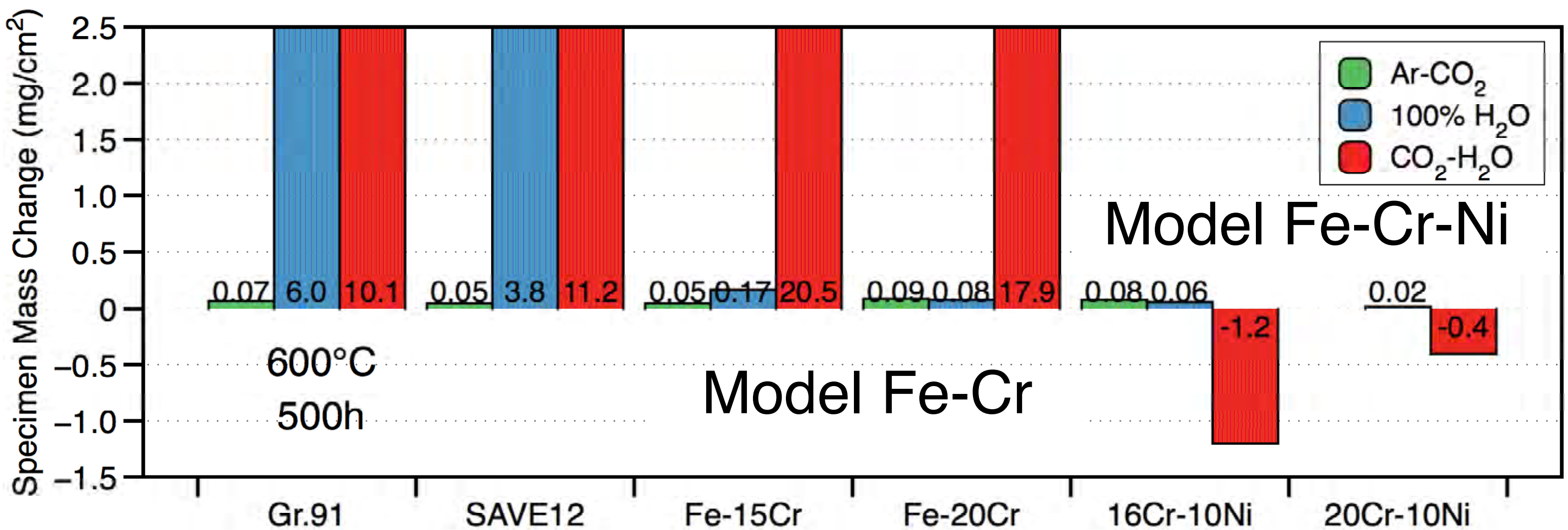
5,000h cross-sections in progress

600°C: H_2O worse than CO_2

Current Quadakkers (Jülich) work (no O buffer)
- concluded that H_2O worse than CO_2

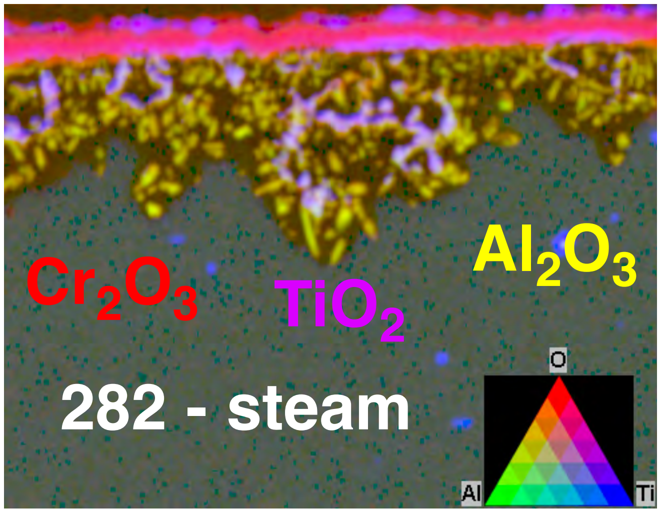
Hypothesis: S and/or H_2O hides ΔCO_2 effect

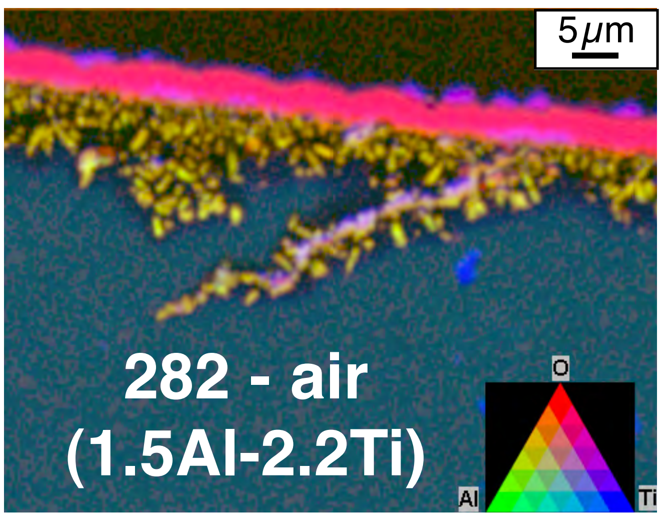
600°C: commercial Fe-Cr (thick oxide in steam)
model Fe-Cr (20%Cr bad in CO_2-H_2O)
model Fe-Cr-Ni (20Cr-20Ni attacked)



800°C steam follow up work

Alloy 282: 5kh in 17bar steam or lab. air



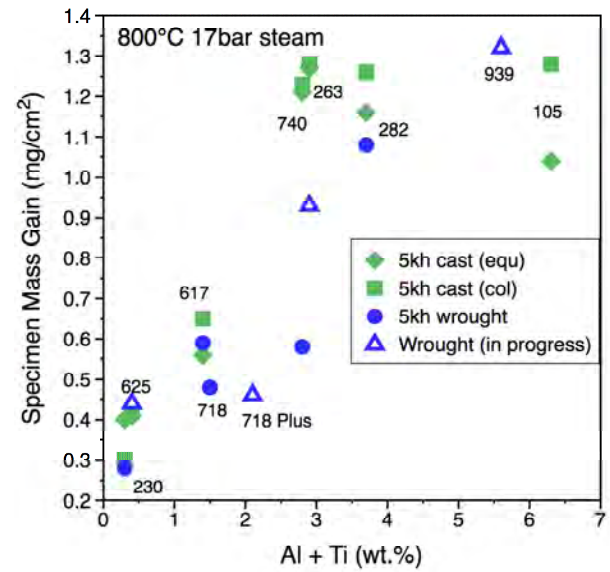


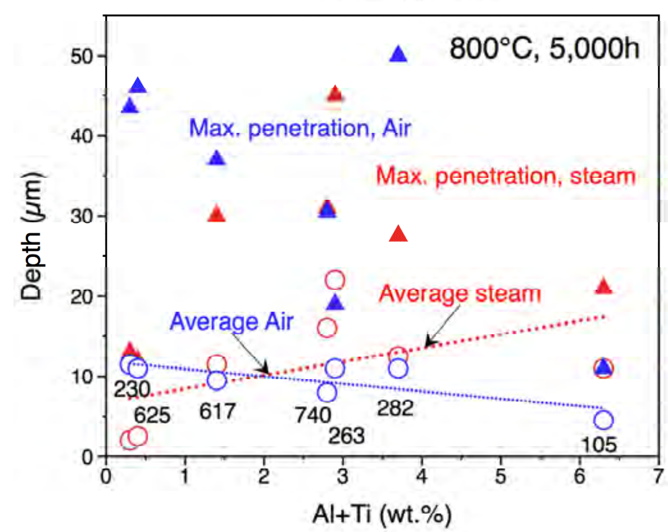
Ni~20Cr

Al+Ti->γ'

Synergy

Al-Ti ?

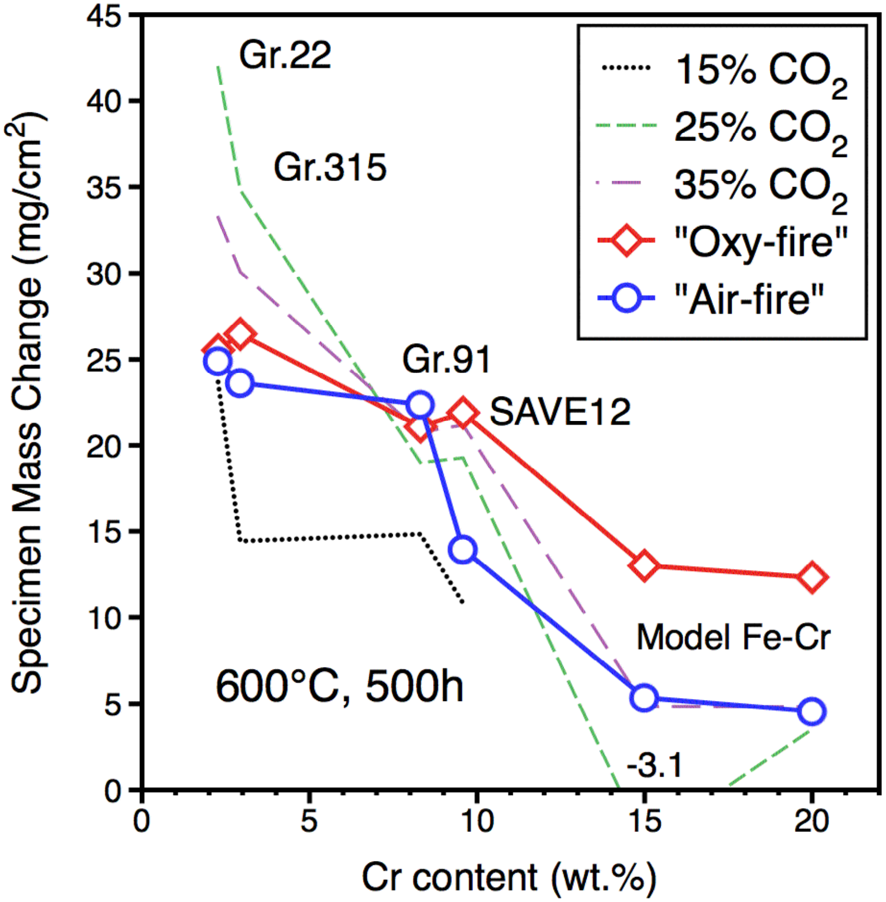




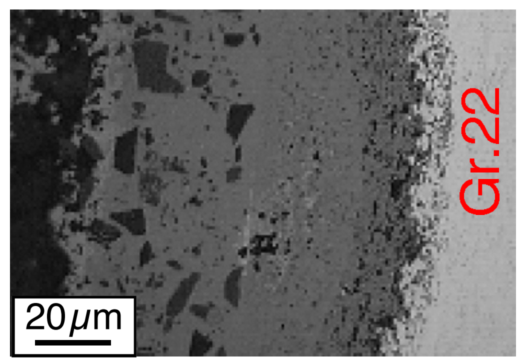
Model alloys: Ni-22Cr + Al +/- Ti in steam

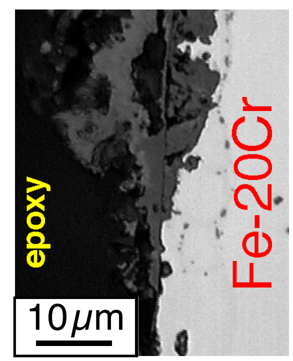
New coal ash tests: H_2O added

Air- and Oxy-firing conditions: 600°C, 500h



	air	O_2
CO_2	16	61%
H_2O	10	32%
O_2	2	2%
SO_2	0.15	0.45%





Modified gas train to add H_2O to test

Mass gain: not a strong effect of H_2O

Change to oxy-firing had strongest effect on high Cr

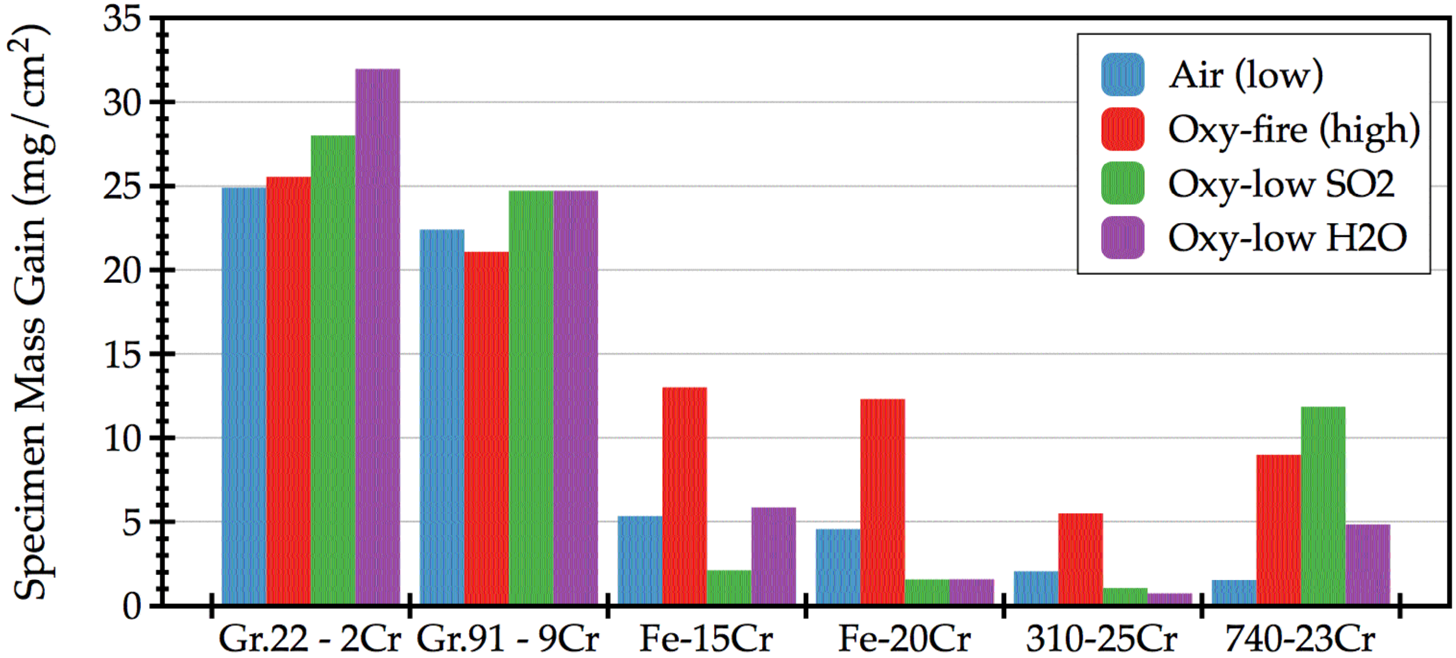
Oxy-firing is more complicated

Bordenet (Alstom) presented worst case
- hot flue gas recycle with no cleaning
  (unlikely, flue gas cools oxy-fired boiler)
- options: cooling flue gas + de-sulfurization

	air-fire	O_2-fire (hot)	(w/FGD) (warm)	(cool)
CO_2	15	61%	61%	83%
H_2O	10	30%	30%	10%
O_2	2	2%	2%	2%
SO_2	0.15	0.45%	0.15%	0.45%

Third series: varied SO_2 and H_2O

Air- and Oxy-firing conditions: 600°C, 500h



2-9Cr: all heavy attack, difficult to quantify

Higher Cr alloys: "oxy" was worst (high SO_2/H_2O)

740 (Ni-23Cr): all oxy (high CO_2) were higher

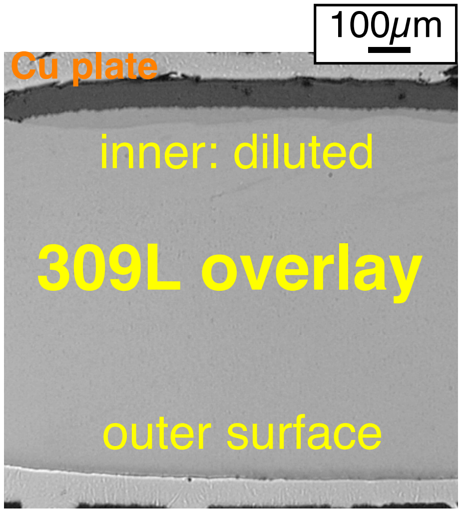
Evaluated weld-overlay coupons

Air- and Oxy-firing conditions: 600°C, 500h

Nominal composition wt.%

from TiNova

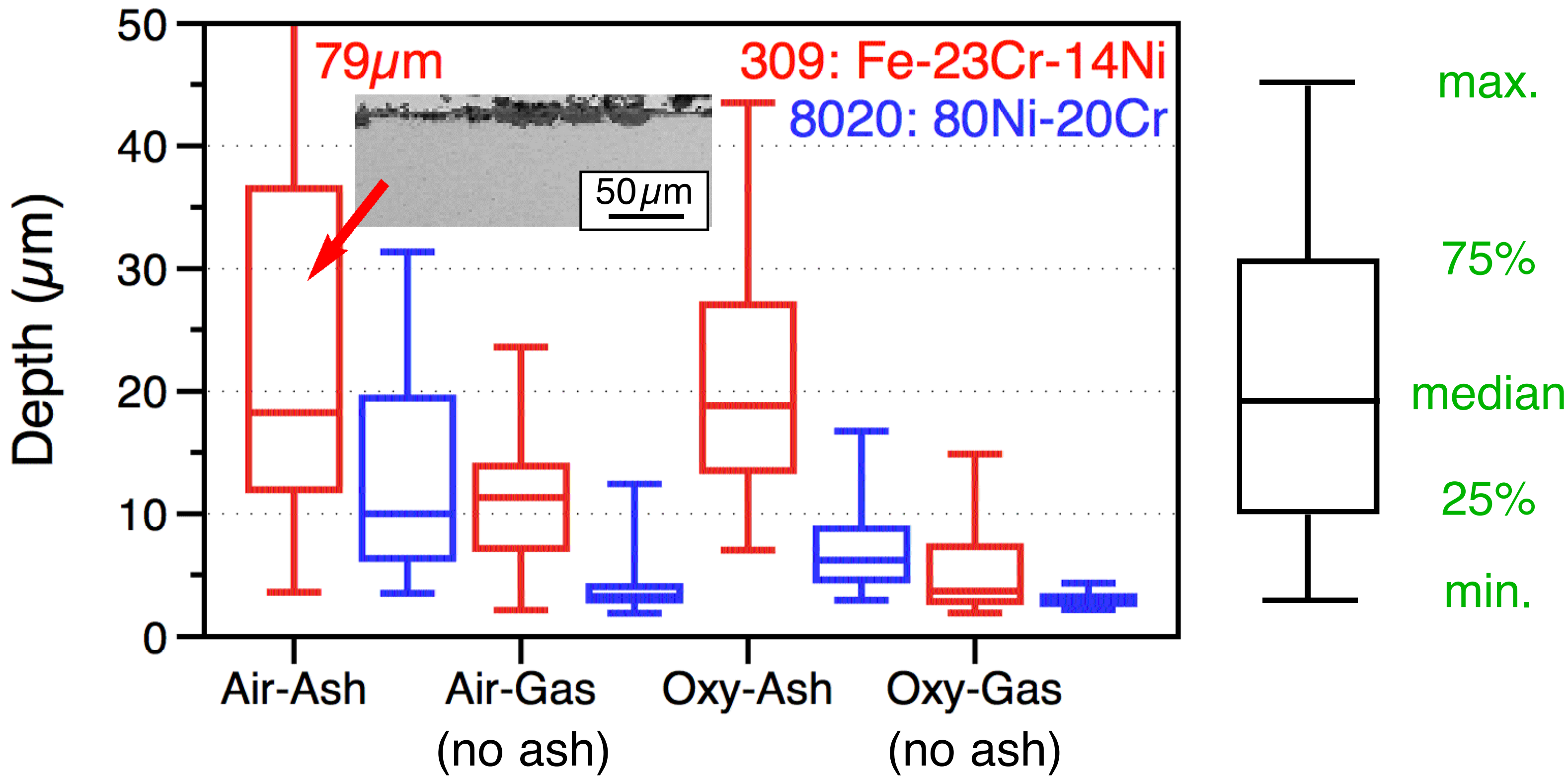
	Fe	Ni	Cr	other
309L	60	14	23	1Mn, 1Si
8020		80	20	
33	33	31	33	2Mo,1Cu
52	9	63	29	
72		57	43	0.3Ti
C22	3	58	23	13Mo,3W



Rectangular coupons: removed overlay from tube
~1mm thick
- face adjacent to substrate has some dilution
- mass change data meaningless

Box plots to quantify attack

Air- and Oxy-firing conditions: 600°C, 500h

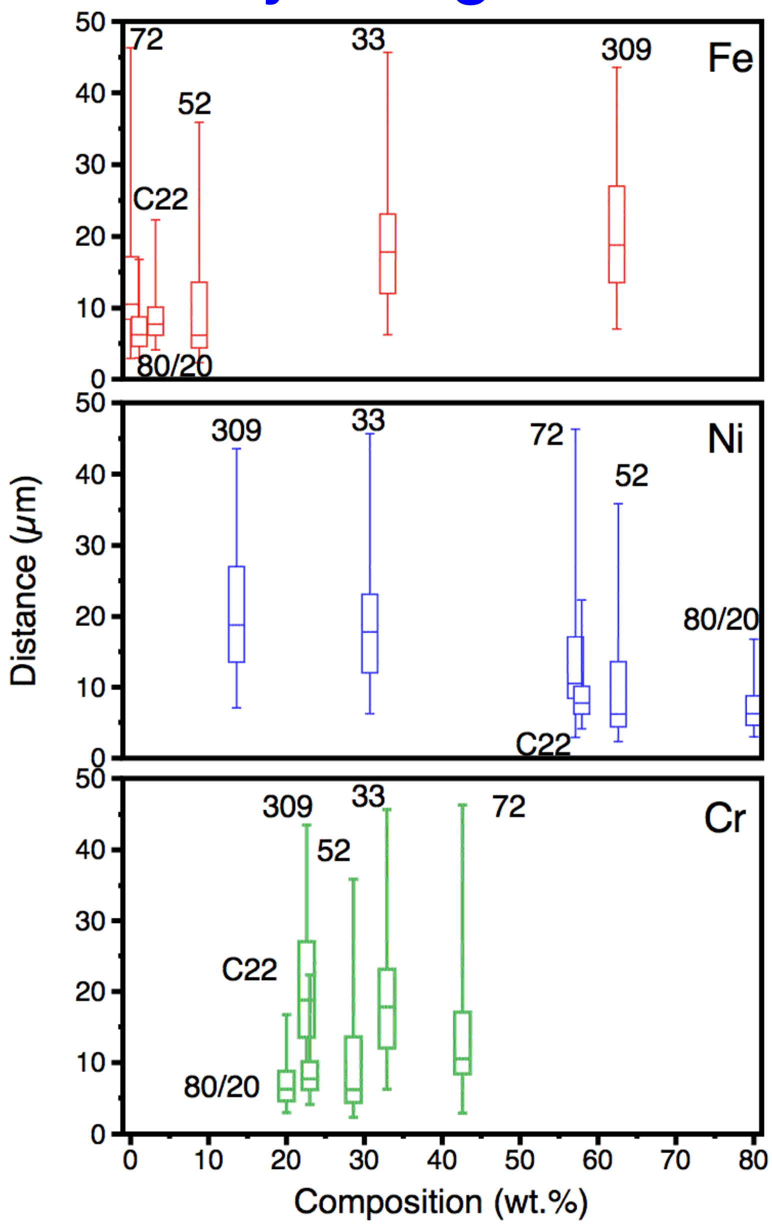


40 data points taken from 500X pictures

- including scale + internal oxidation
- high Ni coating more oxidation resistant
- attack not increased in oxy-firing conditions

Box plots for effect of chemistry

Oxy-firing + ash condition: 600°C, 500h



Commercial coatings:

- Cr content not predictive
- Average:
  - increases with Ni
  - decreases with Fe
- Cr/Ni synergy not clear

Ash experiment issues

Three series of experiments completed:

- ΔCO_2: initial runs without H_2O
- air/oxy: worst case comparison with H_2O
- "milder" oxy-firing: lower H_2O or SO_2

Test protocols to be evaluated:

- use of Pt catalyst (no catalyst running now)
- crucible (covered sample) vs. ash slurry
- cycle frequency 10 x 100h vs. 500h x ?
- goal: "actual" rate or accelerated?

Metal loss measurement

- loss in rod diameter: significant scatter
- box plots capture variable attack

Ash composition: how changed by oxy-firing?

Task 3: effect of steam on creep?

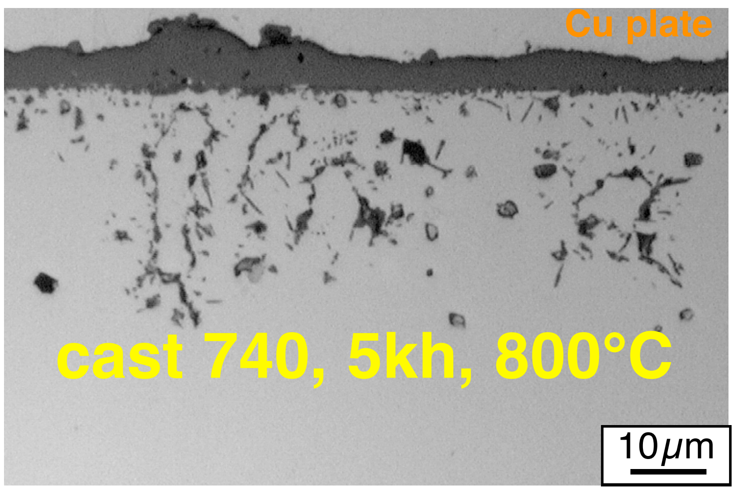
Little experience with new alloys in steam

ex-situ (in air)

in-situ

Creep testing:

- as-received
- after 800°C steam
- after 800°C anneal

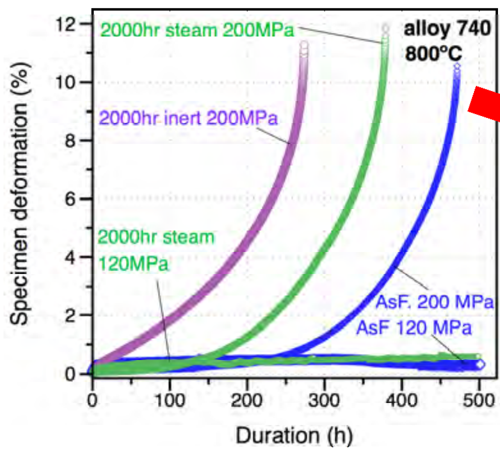


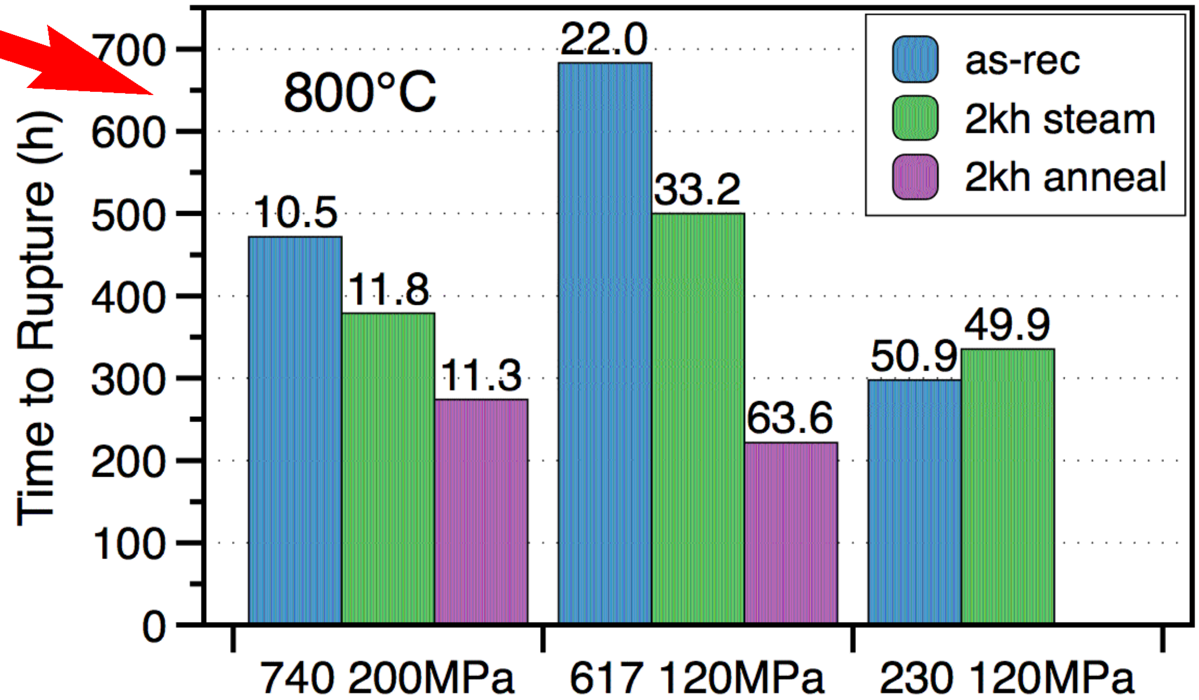
In H_2O, any effect of H injected into metal?

Better comparison: coating debit vs. corrosion debit

Ex-situ testing: anneal vs. steam

2kh anneal to account for thermal effect





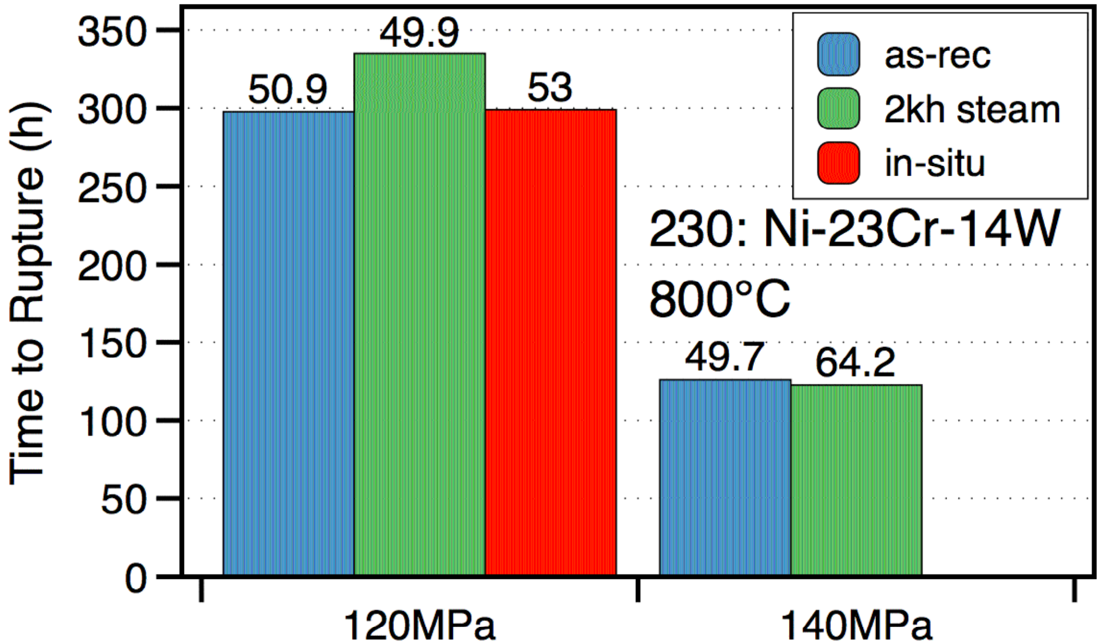
230: no effect of 2kh in steam at 800°C

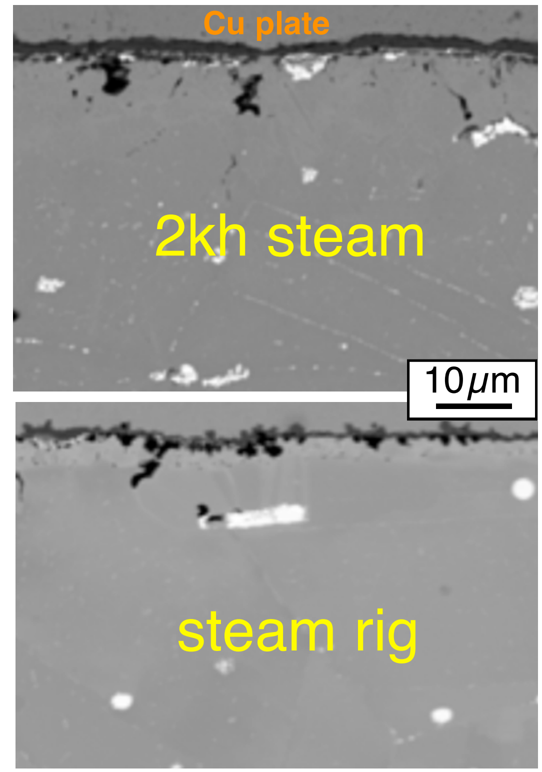
740/617:   decrease life after 2kh steam

larger decrease with 800°C 2kh anneal (?)

Ex-situ vs. in-situ testing: 230

Creep testing in steam at 800°C





230: no effect of 2kh in steam

In-situ creep rupture life similar to life in air

similar ductility

thinner scale - due to strain?

Mechanical testing summary

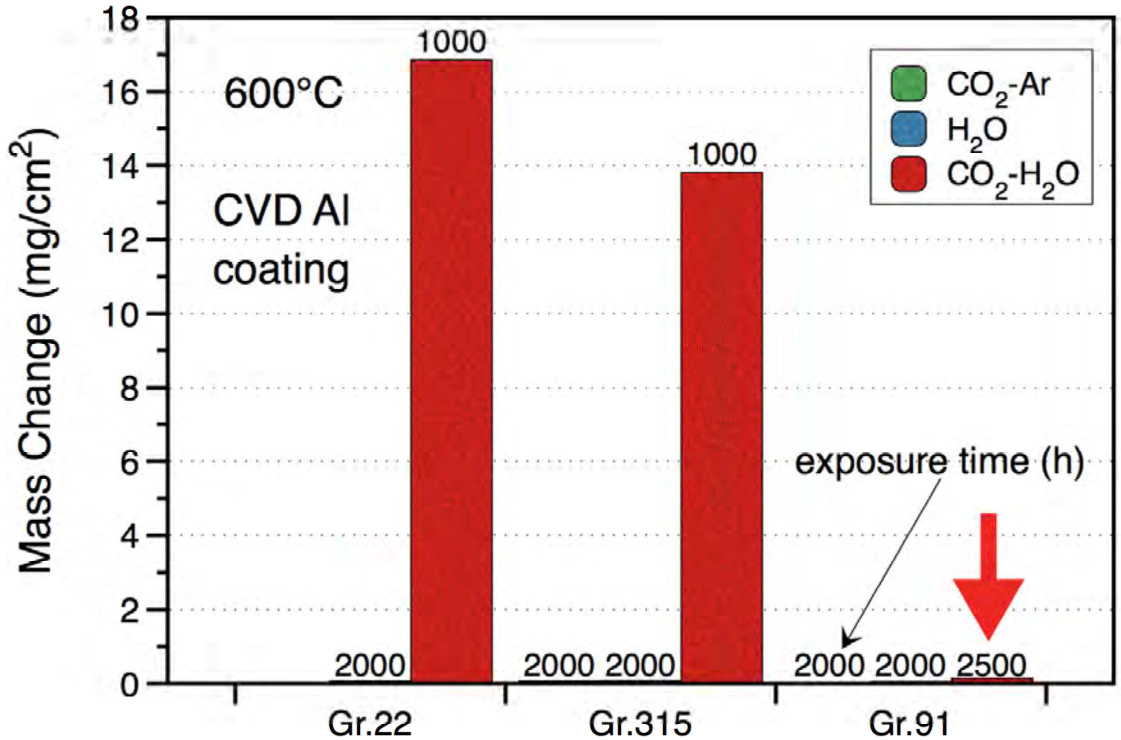
Ex-situ: Ni-base alloys 230, 740, 617, 718
800°C 2 &4 kh steam and anneal
completing matrix in FY11

In-situ: First rig operational (2nd in progress)
No LVDT in alumina tube
Data: rupture time/mode, no long time
Characterize reaction product

Initial work on Ni-base alloys (high interest)
Next move to Fe-base 9-12%Cr

Coating results at 600°C

Low Al content chemical vapor deposition coating



Conclusions:

- Coating prevents thick oxide formation in steam
- Coating less effective on low Cr substrates
- CO_2-H_2O is most aggressive environment

Summary

Four tasks: gas only, with ash, creep, coatings

Completed gas only baseline: 550° & 600°C
- CO_2+H_2O most severe - similar to others

Coal ash corrosion: 600°C 500h exposures
- exploring test parameters
- evaluation of oxy-firing scenarios
- box plots for quantifying metal attack
- overlay coating specimens: oxy not worse

Creep: ex-situ completing, in-situ beginning
- Ni-base: perhaps limited effect of steam

Coatings - model alloys may suggest overlays

CLEAN COAL.
COOL.